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We have compared the metallic evaporation channels from metastable $[Ag_{X=5,7,11}(AgI)_{Y=1-4}]^+$ clusters in the 1st FFR of a double focussing mass spectrometer with that of the corresponding pure metallic clusters, $[Ag_{X=5,7,11}]^+$. It is found that the presence of the polar AgI molecules increases the rate of silver monomer evaporation relative to that of silver dimer evaporation. Using thermodynamic expressions for the heat of evaporation of the different evaporation processes and assuming the absence of reverse activation energies, an expression for the difference between the activation energy of silver monomer and dimer evaporation is derived. It is shown that dipole/induced-dipole forces resulting from the presence of AgI polar molecules lead to an enhancement of silver monomer evaporation if the polarizability of the pure metallic cluster ions increases with the number of Jellium electrons. Our theoretical calculations of the static polarizabilities of $[Ag_X]^+$, using time dependent density functional theory within the local density approximation, shows a smooth increase in the polarizabilities with the number of the Jellium electrons in these clusters. Finally, we observe that the enhancement of Ag monomer evaporation per AgI added is smaller for clusters with even number of AgI molecules than with odd numbers. This was proposed to result from the contribution of configurations with dipole "pairing" of the AgI molecules in clusters with even number of AgI molecules. Dipole pairing would decrease the average dipole/induced-dipole interaction between the AgI molecules and the metallic part of these "mixed" clusters.

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ADHESION OF POLAR MOLECULES TO SILVER NANOCUSTER IONS**

by

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THE ENHANCEMENT OF METALLIC SILVER MONOMER EVAPORATION BY THE ADHESION OF POLAR MOLECULES TO SILVER NANOCUSTER IONS

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Abstract

We have compared the metallic evaporation channels from metastable $[\text{Ag}_{X=5,7,11}(\text{AgI})_{Y=1-4}]^+$ clusters in the 1st FFR of a double focussing mass spectrometer with that of the corresponding pure metallic clusters, $[\text{Ag}_{X=5,7,11}]^+$. It is found that the presence of the polar AgI molecules increases the rate of silver monomer evaporation relative to that of silver dimer evaporation. Using thermodynamic expressions for the heat of evaporation of the different evaporation processes and assuming the absence of reverse activation energies, an expression for the difference between the activation energy of silver monomer and dimer evaporation is derived. It is shown that dipole/induced-dipole forces resulting from the presence of AgI polar molecules lead to an enhancement of silver monomer evaporation if the polarizability of the pure metallic cluster ions increases with the number of Jellium electrons. Our theoretical calculations of the

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static polarizabilities of $[Ag_x]^+$, using time dependent density functional theory within the local density approximation, shows a smooth increase in the polarizabilities with the number of the Jellium electrons in these clusters. Finally, we observe that the enhancement of Ag monomer evaporation per AgI added is smaller for clusters with even number of AgI molecules than with odd numbers. This was proposed to result from the contribution of configurations with dipole "pairing" of the AgI molecules in clusters with even number of AgI molecules. Dipole pairing would decrease the average dipole/induced-dipole interaction between the AgI molecules and the metallic part of these "mixed" clusters.

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I. INTRODUCTION

Metal/metal halide clusters are particularly fascinating systems to study because of their electronically heterogeneous character. These clusters provide unique opportunities for studying the binding forces between the metallic and ionic phases on the molecular level. Many properties of monovalent metal (Group IA and IB) clusters have been found to be size-dependent. Relative stabilities¹⁻⁴, ionization potentials^{1,2,5}, electron affinities⁶, and static polarizabilities⁷, collective excitation frequencies⁸, are all found to be described in terms of the Spherical Jellium Model (SJM)⁹. SJM has successfully predicted the physical properties of alkali and noble metal clusters by assuming that a cluster's properties are determined by the number of delocalized valence electrons which occupy the predicted shell structure. Any deficiencies of SJM stem from its simplifying assumptions, i.e. the electrons move in a positive uniform background potential and the neglect of core/valence electron interactions.

The first experimental measurements of the polarizability of alkali metal clusters showed, for some cluster sizes, results which did not conform to Jellium model predictions.⁷ It was suggested then and later supported by theoretical calculations¹⁰ that the anomalous polarizabilities could be accounted for by assuming that a size dependent transition occurred between a two dimensional to a three dimensional structure. A 2-D to 3-D transition would effectively decrease the polarizability while SJM predictions would have predicted an increase.

Giant resonance absorption frequencies have recently been measured for gas phase $[\text{Ag}_x]^+$ clusters by photodepletion techniques⁸ and for $[\text{Ag}_x]$ clusters in rare gas matrices.¹¹ Both studies show maxima in the resonance absorption frequencies for closed shell clusters, i.e. $[\text{Ag}_9]^+$ or $[\text{Ag}_8]$ ($1s^2, 1p^6$) and $[\text{Ag}_{19}]^+$ or $[\text{Ag}_{19}]$ ($1s^2, 1p^6, 1d^{10}$). In confluence with these measurements, theoretical calculations¹² predict a minima in the polarizabilities of clusters for the Jellium electronic configuration: $1s^2, 1p^6$ and $1s^2, 1p^6, 1d^{10}$, respectively.

Studies of "mixed" metallic/ionic clusters for the alkali metals have been carried out for $\text{Cs/Cs}_2\text{O}$ ¹³ and Na/NaCl ¹⁴ clusters. Whetten and coworkers¹⁵ have estimated the binding

energy of an excess electron in slightly metal-rich alkali halide clusters as well as metallization of purely ionic clusters by photo-induced ejection of halogen atoms.¹⁶ Rabin et. al.¹⁷ have generated non-stoichiometric metal-rich AgF clusters by the inert aggregation technique. From their relative mass intensities they have suggested a cluster structure composed of a metallic "core" encased in a "shell" of fluorine anions.

In a recent paper,¹⁸ we examined the relative evaporation probabilities for AgI molecules from metastable $[\text{Ag}_x(\text{AgI})_y]^+$ clusters. In that paper, we observed a change in the relative evaporative loss of AgI from clusters whose metallic part possessed an "open" vs. "closed" Jellium electronic configuration. We suggested that the difference in the static polarizabilities of "open" vs. "closed" metallic shells may contribute to the binding energy of individual AgI molecules in $[\text{Ag}_x(\text{AgI})_y]^+$ clusters through dipole/induced-dipole forces. We also observed a unique dissociative loss among these clusters: $(\text{AgI})_3$ loss from $[\text{Ag}_{12}\text{I}_3]^+$ (structurally written as $[\text{Ag}_9^+(\text{AgI})_3]$). Since the metallic part of $[\text{Ag}_9^+(\text{AgI})_3]$ has a *low* polarizability due to its SJM shell closing, we suggested that weak dipole/induced-dipole forces lead to $(\text{AgI})_3$ formation followed by a "fission" process into $[\text{Ag}_9]^+$ and $(\text{AgI})_3$. We could not, however, exclude the possibility that the high metallic stability of $[\text{Ag}_9]^+$ may also contribute to the evaporative loss of $(\text{AgI})_3$. It is difficult to isolate the effects of metallic stability and metallic polarizability in the binding of metastable $[\text{Ag}_x\text{I}_y]^+$ clusters from evaporative loss of $(\text{AgI})_y$.

In the current paper, we avoid this difficulty by noting that metallic stability and metallic polarizability are physical properties which, in jellium clusters, anti-correlate. In other words, a jellium cluster that has high stability also has low polarizability, and vice versa. The unimolecular dissociation of metastable $[\text{Ag}_x]^+$ clusters are determined by the relative stability of the dissociation products resulting from competing evaporative channels: Ag monomer and Ag_2 loss. If dipole/induced-dipole forces are present in $[\text{Ag}_x(\text{AgI})_y]^+$ clusters, then we might expect to see some alteration of the metallic evaporative channels compared with the evaporation channels of $[\text{Ag}_x]^+$ clusters.

The clusters we have selected for our study are $[\text{Ag}_X(\text{AgI})_Y]^+$ for $X = 5, 7$ and 11 . The pure metal part of these clusters i.e. for $Y = 0$; show dominance of Ag_2 evaporation and a very low probability of Ag monomer loss. These type of clusters would thus be suitable for detecting the enhancement in the probability of the monomer loss in the presence of AgI molecules, if such perturbation would take place. We further like to examine if this enhancement is correlated to the polarizability of the pure metallic clusters as well as the size of the effective dipole moment of the AgI molecules added. We have derived an expression for the difference between the activation energy for the monomer and the dimer evaporation processes. This is found to depend on the difference between the polarizability of the metallic cluster daughter ions resulting in the two evaporation processes.

We have calculated the polarizabilities of $[\text{Ag}_X]^+$ using Density Functional Theory within the Local Density Approximation (TDLDA) for SJM. From these calculations, we compare the metallic evaporation channels of $[\text{Ag}_{X=5,7,11}]^+$ vs. $[\text{Ag}_{X=5,7,11}(\text{AgI})_{Y=1}]^+$ clusters with the expected effects of the dipole/induced-dipole coupling as determined by the polarizabilities of the $[\text{Ag}_X]^+$ clusters. We find good agreement between calculated polarizabilities and the evaporative channels observed. Finally, we have observed that the enhancement of Ag monomer loss (per AgI) is higher for clusters with odd number of AgI molecules than those with even number. This may result from the contribution of configurations having "paired" AgI dipoles in clusters with an even number of AgI molecules. This leads to a reduced average dipole/induced-dipole interaction and an enhancement factor in these clusters.

The layout of the paper is as follows: In Section II we give details of the experimental set-up. Section III, gives the experimental observations and discusses them in terms of the activation energies of the processes involved. Appendix I gives the details of the theoretical model used in calculating the polarizabilities of the silver cluster ions.

II. EXPERIMENTAL

The experimental set-up was described in a previous paper.^{19a} Briefly, the instrument used in our experiments is a VG Analytical ZAB-70 SE double focussing mass spectrometer ("reverse" geometry) fitted with a fast atom bombardment gun (Model FAB11N, Ion Tech Ltd., Teddington, Middlesex, UK). Isotopically enriched silver foil which is 98.54% ^{107}Ag , of dimensions 3×10 mm, was mounted on a FAB probe tip and inserted into the source region.

The foil was sputtered with the FAB gun typically at 7.0 kV with a discharge current of 1.4 mA. Methyl iodide vapor was introduced into the source region from a heated diffusion port at a temperature of 100°C . The methyl iodide vapor effusing out of the diffusion port forms a vapor jet, part of which is directed toward the sputtered silver foil although the methyl iodide is dispersed generally throughout the entire chamber. Upon introduction of the methyl iodide, the base pressure in the source region increased from $(5.0\text{--}7.0) \times 10^{-6}$ mBar (xenon FAB gas) to $(2.0\text{--}3.0) \times 10^{-5}$ mBar as read continuously during the experiment from an ion gauge located above the source chamber diffusion pump. Scanning and data collection were run with the commercial software provided with the instrument. Individual scans were summed and divided by the number of scans to produce 10 scan averages. The mass range was 100-2300 AMU at a scan rate of 40.0 sec/mass decade (56.5 sec/scan). There was a 5 second delay between each scan.

Our instrument has ion acceleration voltages: $V_{\text{Acc}} = 3, 4, 5, 6, 7, 8, 9$ and 10-kV. Unfortunately, metastable $[\text{Ag}_x\text{I}_y]^+$ signal (which is significantly weaker in intensity than stable $[\text{Ag}_x\text{I}_y]^+$ signal) becomes progressively weaker as V_{Acc} is reduced due to space charge effects and poor ion focussing. We observe large fluctuations in metastable signal intensity and consequently large error bars in relative evaporation channels below $V_{\text{Acc}} = 7$ kV. In consequence, metastable ion signal was collected at two ion accelerations (8.13 kV and 10.16 kV) in order to compare the difference, if any, of the metallic evaporation channels as a function of ion flight time.

Dissociation of metastable ions in the first field free region (1st FFR) of this instrument were studied using Constant Neutral Mass Loss Scanning (CNML), a "linked" mass spectrometry scanning technique. A "link" scan involves scanning both magnetic and electric sectors simultaneously such that the ratio of the strength of the magnetic field to that of the electric field corresponds to a fixed mathematical ratio (B/E , B^2/E , etc.). The three most common "link" scanning techniques are:

1. Daughter Ion Scanning ($B/E = \text{constant}$);
2. Parent Ion Scanning ($B^2/E = \text{constant}$);
3. Constant Neutral Mass Loss Scanning ($B(1-E)^{1/2}/E = \text{constant}$).

In the present work, we used CNML in studying the unimolecular dissociation of metastable cluster ions in the 1st FFR of our instrument.

CNML was first developed²⁰ with the hope of identifying unknown organic compounds based on characteristic functional groups lost after ionization. We have found it to be an efficient technique in studying the unimolecular dissociation of metastable $[\text{Ag}_x\text{I}_y]^+$ clusters. Given the number of stable and metastable $[\text{Ag}_x(\text{AgI})_y]^+$ ions generated in our instrument, it is difficult to identify individual metastable peaks exclusively by their "apparent" mass in the 1st FFR because two or more metastable peaks may have overlapping "apparent" masses. There is also overlapping between metastable and stable cluster ion peaks (cluster ions that leave the source without further dissociation). The overlap problem is avoided with "link" scanning where the parent ion and daughter ion are uniquely identified by the evaporative channel. Previously overlapping metastable peaks are discriminated by the neutral fragment evaporated, and stable cluster ions are screened out by the electric sector because they have not undergone a dissociation. Another advantage of CNML Scanning is that in a single scan one detects all metastable clusters that have undergone a specified evaporative loss. Thus, CNML Scanning is a very useful scanning technique for studying the unimolecular dissociation of metastable $[\text{Ag}_x\text{I}_y]^+$ clusters. A disadvantage with CNML Scanning (as well as Daughter Ion Scanning) is that the kinetic energy release (KER) of the dissociation is lost because of the high resolution

nature of the technique. Daughter ions, whose KER exceeds the resolution of the instrument, are “filtered” by the electric sector. To minimize any loss of metastable ion signal, the resolution of the instrument was kept as low as possible: $m/\Delta m = 700$.

We briefly outline the mathematical relationship relating a specified neutral loss from an unspecified parent ion. If we have a dissociation in the 1st FFR such that,

$$m_p^+ \rightarrow m_d^+ + m_n \quad (1)$$

m_d^+ will have an “apparent” mass²¹ in the 1st FFR region:

$$m^* = \frac{m_d^2}{m_p} = \frac{B^2 R^2}{2V_{Acc}} \quad (2)$$

where m^* is the “apparent” mass of m_d , B is the magnetic field strength, R is the radius of the magnetic, V_{Acc} is the acceleration voltage. To pass the ion m_d^+ through the electric sector, the electric field strength is “uncoupled” from the acceleration voltage and altered to a strength proportional to the mass ratio of m_d^+ and m_p^+ :

$$E = \frac{m_d}{m_p} = 1 - \frac{m_n}{m_p} \quad (3)$$

If we write m_p and m_d in terms of m_n and substitute we obtain the following expression²²:

$$\frac{B}{E}(1-E)^{1/2} = \frac{(2V_{Acc}m_n)^{1/2}}{R} \quad (4)$$

Thus for a constant $B(1-E)^{1/2}/E$, a fixed V_{Acc} and the fixed radius of the magnet, we detect all metastable ions that dissociate by evaporative loss of the specified neutral, m_n .

III. RESULTS AND DISCUSSION

A. Experimental Results

The top panel of Figures 1-3 show the relative evaporative channels for the unimolecular dissociation of metastable $[\text{Ag}_{X=5}(\text{AgI})_{Y=0-3}]^+$, $[\text{Ag}_{X=7}(\text{AgI})_{Y=0-3}]^+$, and $[\text{Ag}_{X=11}(\text{AgI})_{Y=0-4}]^+$ clusters, respectively, in the 1st FFR of our instrument at an acceleration voltage of 10.16 kV. Y denotes the number of AgI molecules in the parent cluster ion. A detailed discussion of the AgI evaporative channel has been presented in a previous paper.¹⁸ The middle panel of Figures 1-3 show the relative metallic evaporative channels, i.e. those clusters which dissociate by a metallic evaporative channel. Clusters which undergo a metallic evaporative loss have the same number of AgI molecules in the parent cluster ion as in the daughter cluster ion. Finally, the bottom panel of Figures 1-3 shows Ag monomer loss *per* AgI obtained by dividing Ag monomer loss in the middle panel by the number of AgI in the cluster. Each data point in Figures 1-3 is an average of five experiments. Each experiment is an average of ten scans of the mass range. Error bars denote the standard deviation in five experiments. Figure 4 is a "normal" scan mass spectra of stable $[\text{Ag}_x]^+$ clusters.¹⁹ The relative intensity of neighboring clusters reflect their relative stability. Note SJM shell closings ("magic" numbers) at $[\text{Ag}_3]^+$ ($1s^2$) and $[\text{Ag}_9]^+$ ($1s^2, 1p^6$). Odd/even oscillation for "open" shell clusters are also prominent. $[\text{Ag}_{X=5,7,11}]^+$ are marked by an asterisk.

B. Evaporative Channels of Metastable $[\text{Ag}_{X=5,7,11}]^+$

The unimolecular dissociation of metastable clusters may be described as evaporative dissociations of vibrationally excited clusters through the lowest energy evaporative channels. We selected metastable $[\text{Ag}_{X=5,7,11}(\text{AgI})_{Y=0-4}]^+$ clusters for study because metastable $[\text{Ag}_{X=5,7,11}]^+$ are the only $[\text{Ag}_x]^+$ clusters which dissociate almost exclusively by evaporative

loss of Ag_2 (> 95%). Our instrument does not distinguish between sequential loss of two Ag monomers vs. Ag_2 , however dimer loss is the accepted evaporation fragment on the basis of SJM²³ calculations as well as statistical evaporation dynamics.²⁴ The effect of AgI dipole(s) on the metallic evaporation channels should be more prominent for $[\text{Ag}_{X=5,7,11}]^+$ than other $[\text{Ag}_{X=\text{odd}}]^+$ clusters where Ag monomer loss is a major evaporative channel. Finally, $[\text{Ag}_{X=\text{even}}]^+$ clusters evaporate exclusively by Ag monomer loss which is also found to be the case for $[\text{Ag}_{X=\text{even}}(\text{AgI})_{Y=1-4}]^+$ clusters. Thus, a study of the dissociation of $[\text{Ag}_{X=\text{even}}(\text{AgI})_{Y=0-4}]^+$ clusters tell us very little about metallic-ionic interactions.

We begin first with a comparison of the unimolecular dissociation channels of metastable $[\text{Ag}_{X=5,7,11}]^+$ clusters. The results are summarized in Table I. As previously mentioned, $[\text{Ag}_{X=5,7,11}]^+$ dissociate almost exclusively by Ag_2 loss. Our results are very similar to experimental results obtained by Brechignac et al.²⁴ for metastable $[\text{Na}_X]^+$ clusters where Na_2 loss was the exclusive evaporative channel of $[\text{Na}_{X=5,7,11}]^+$. It is straightforward to rationalize M_2 loss as the dominant evaporative channel of metastable $[\text{M}_{X=5,7,11}]^+$ clusters on the basis of SJM predictions. SJM gives a good starting framework to understand these evaporative channels through a direct energetic balance argument.^{23,25} The daughter ions formed from M_2 loss have "closed" Jellium shells (CS) and are thus predicted by SJM to have high stability. The only exception is $[\text{M}_7]^+$ which undergoes M_2 loss to produce the daughter ion $[\text{M}_5]^+$. $[\text{M}_5]^+$ has the SJM electronic configuration: $1s^2, 1p^2$ (which is not a "closed" shell configuration). However, it is known,²⁶ for "open" shell Jellium clusters, that Jahn-Teller splitting of the degenerate orbitals ($1p_x, 1p_y, 1p_z$) favors the stability of even-electron clusters. The effect of this energy splitting is evident from the relative intensity of $[\text{Ag}_5]^+$ and $[\text{Ag}_6]^+$ in the "normal" scan spectra of stable $[\text{Ag}_X]^+$ clusters shown in Figure 4. Thus, the predominance of the Ag_2 evaporative loss from metastable $[\text{Ag}_{X=5,7,11}]^+$ clusters is due to the relative stability of $[\text{Ag}_{X=3,5,9}]^+$ compared with the relative instability of $[\text{Ag}_{X=4,6,10}]^+$.

Brechignac et. al.²⁴ have calculated the dissociation energies of metastable $[\text{Na}_X]^+$ clusters from their evaporative channels, Na monomer and Na_2 , and using a modified RRK

theory by Engelking.²⁷ The modified RRK requires a very accurate KER in order to obtain accurate binding energies. As mentioned in the experimental section, CNML scanning does not allow measurement of the KER because of the high resolution nature of the scanning technique. Thus, we cannot estimate the binding energies of $[\text{Ag}_x]^+$ using this scanning technique. We are currently attempting to estimate the binding energies of metastable $[\text{Ag}_x]^+$ from their unimolecular dissociation in the 1st FFR using "normal" scanning in the single focus mode. Single focus mode scanning allows for measurement of the KER, however it does not discriminate overlapping peaks.

We investigated these dissociations at two acceleration voltages in order to examine the effect of cluster "temperature" on the relative dissociation patterns of Ag monomer vs. Ag_2 loss. The higher acceleration of 10.16 kV should detect dissociations from clusters that are, on average, vibrationally "hotter" than the dissociations we detect at 8.13 kV. Clusters generated by sputtering undergo evaporative dissociations as soon as they leave the sample surface. The longer the time between their cluster formation and entering the 1st FFR, the more dissociations have occurred. A higher source acceleration should sweep a larger proportion of vibrationally "hotter" metastable clusters into the 1st FFR. The results at $V_{\text{Acc}} = 10.16$ kV and $V_{\text{Acc}} = 8.13$ kV were within the error bars of the two experiments. Thus, we do not observe any significant change in Ag monomer vs. Ag_2 loss for the two accelerations. This may suggest that the average "temperature" of the metastable clusters are not significantly affected by the change in acceleration although at 10.16 kV the ion flight time is shortened by $\approx 10\%$ over that at 8.13 kV. Another possibility is that the evaporation of Ag monomer vs. Ag_2 may be relatively insensitive to variations in cluster "temperature" (e.g. have similar activation barriers). Recent theoretical calculations on the stability of copper clusters at elevated temperatures have shown that clusters with an SJM shell closing retain their stability even at elevated temperatures.²⁸ The Jellium electronic levels (and any physical properties dependent on such levels) may be relatively insensitive to cluster internal energy.

C. The Effect of Polar AgI Molecules on the Metallic Evaporation from



We now examine the metastable clusters which have a single AgI molecule in the cluster: $[\text{Ag}_X(\text{AgI})_{Y=1}]^+$ (Figures 1, 2 and 3: $Y=1$). These clusters show an increase in Ag monomer loss compared with the purely metallic clusters ($Y=0$). The largest increase is found for $[\text{Ag}_{X=7}(\text{AgI})_{Y=1}]^+$ and the smallest for $[\text{Ag}_{X=7}(\text{AgI})_{Y=1}]^+$. $[\text{Ag}_{X=11}(\text{AgI})_{Y=1}]^+$ clusters appear to be nearly comparable to $[\text{Ag}_{X=7}(\text{AgI})_{Y=1}]^+$. One might argue that the increase in Ag monomer loss for $[\text{Ag}_{X=5,7,11}(\text{AgI})_{Y=1}]^+$ compared with $[\text{Ag}_{X=5,7,11}]^+$ may be a "temperature" effect. However, one would expect such an effect to scale with the number of AgI in the cluster, i.e. the greater the number of AgI, the greater the internal energy of the cluster and the greater the loss of Ag monomer. However, we find upon addition of a second AgI, i.e. $[\text{Ag}_{X=5,7,11}(\text{AgI})_{Y=2}]^+$ a decrease in Ag monomer loss for all clusters except $[\text{Ag}_{X=11}(\text{AgI})_{Y=2}]^+$ (which shows a decline in Ag monomer loss per AgI - Figure 3 - bottom panel). For metastable clusters with three AgI ($Y = 3$), we observe either an increase in Ag monomer loss or no change compared with $Y = 2$. The metastable ion signal of $[\text{Ag}_{X=5,7}(\text{AgI})_{Y=4}]^+$ was too weak to obtain accurate values. We detected the dissociation of $[\text{Ag}_{X=11}(\text{AgI})_{Y=4}]^+$ but with large fluctuations as shown from the error bars.

The oscillation in the metallic channels as a function of AgI suggests that the effect of AgI(s) is not due to a vibrational excitation of the cluster. The observed oscillation could result from pairing effect of the dipoles of the AgI molecules in clusters with even number of AgI dipoles. In these clusters, the contribution of configurations in which the individual dipoles (or their effect) exactly cancels. This leads to a decrease in the average of the effective permanent dipole moment or decrease their effect in enhancing monomer evaporation.

D. Enthalpy of Evaporation of Ag Monomer and Ag₂ from [Ag_x(AgI)]⁺ Clusters:

Assuming that:

$$H_{Ag_x^+ \cdot AgI}^{Form} = H_{Ag_x^+}^{Form} + H_{AgI}^{Form} + H_{(Ag_x^+)(AgI)}^{Int}$$

where $H_{Ag_x^+ \cdot AgI}^{Int}$ is the dipole/induced-dipole interaction energy between Ag_x^+ and the AgI molecule. The enthalpy of evaporation of a neutral fragment, Ag_y, from [Ag_x(AgI)]⁺, is then given by the following equation:

$$\Delta H_{Ag_y}^{Evap} = [H_{(Ag_{x-y}^+)}^{Form} + H_{AgI}^{Form} + H_{(Ag_{x-y}^+)(AgI)}^{Int} + H_{Ag_y}^{Form}] - [H_{(Ag_x^+)}^{Form} + H_{AgI}^{Form} + H_{(Ag_x^+)(AgI)}^{Int}] \quad (9)$$

Rearranging Eq. 9, we obtain:

$$\Delta H_{Ag_y}^{Evap} = [H_{(Ag_{x-y}^+)}^{Form} - H_{(Ag_x^+)}^{Form} + H_{Ag_y}^{Form}] + [H_{(Ag_{x-y}^+)(AgI)}^{Int} - H_{(Ag_x^+)(AgI)}^{Int}] \quad (10)$$

or

$$\Delta H_{Ag_y}^{Evap} = \Delta H_{(Ag_{x-y}^+)-(Ag_x^+)}^{Form} + H_{Ag_y}^{Form} + \Delta H_{(Ag_{x-y}^+)(AgI)-(Ag_x^+)(AgI)}^{Int} \quad (11)$$

Given the highly polarizable electron density of metallic jellium clusters⁷, we assume that $H_{(Ag_{x-y}^+)(AgI)}^{Int}$ and $H_{(Ag_x^+)(AgI)}^{Int}$ results from dipole/induced-dipole forces between the permanent dipole moment of AgI and the delocalized electron density of the metallic part of the cluster. A dipole/induced-dipole interaction between a single AgI molecule and [Ag_x]⁺ is given by:

$$H_{(Ag_x^+)(AgI)}^{Int} = \frac{(\mu_{AgI}^2) (\alpha_{Ag_x^+})}{4\pi\epsilon_0 R^6} \quad (12)$$

where $\mu_{AgI} = 5.10 \text{ D}$,²⁹ $\alpha_{Ag_x^+}$ is the polarizability of $[Ag_x]^+$, R is the separation between AgI and $[Ag_x]^+$ and ϵ_0 is the permittivity constant. Note that the dipole/induced-dipole force is independent of temperature. If we assume that R and μ_{AgI} are similar in $[(Ag_x^+)(AgI)]$ and $[(Ag_{x-y}^+)(AgI)]$, then $\Delta H_{(Ag_{x-y}^+)(AgI)-(Ag_x^+)(AgI)}^{Int}$ in Eq. 11 is linearly proportional to $\Delta\alpha_{(Ag_{x-y}^+)-(Ag_x^+)}$, i.e. the difference in the polarizability of $[Ag_{x-y}]^+$ and $[Ag_x]^+$.

We are interested in the competitive evaporation between Ag monomer and Ag_2 from metastable $[Ag_{x=5,7,11}(AgI)]^+$ clusters. Thus, we are interested in the difference in energy between the evaporation of Ag monomer and the evaporation of Ag_2 . If we substitute $Y = 1$ (Ag monomer loss) and $Y = 2$ (Ag_2 loss) in Eq. 10 and subtract one from the other, the parent cluster ion terms cancel, and we obtain:

$$[\Delta H_{Ag}^{Evap} - \Delta H_{Ag_2}^{Evap}] = [H_{(Ag_{x-1}^+)}^{Form} - H_{(Ag_{x-2}^+)}^{Form}] + [H_{Ag}^{Form} - H_{Ag_2}^{Form}] + [H_{(Ag_{x-1}^+)(AgI)}^{Int} - H_{(Ag_{x-2}^+)(AgI)}^{Int}] \quad (13)$$

If the condensation reactions of Ag or Ag_2 onto the $(Ag_{x-1}^+) \cdot AgI$ and $(Ag_{x-2}^+) \cdot AgI$ clusters, respectively, are barrierless, the difference in the heats of evaporation in equation (13) is equal to the difference in the activation energies of the corresponding evaporation processes ($E_1^a - E_2^a$). Substituting D_1 and D_2 for Ag_{x-1}^+ and Ag_{x-2}^+ respectively, and rearranging equation (13), one obtains:

$$(E_1^a - E_2^a) = E_{Mon}^a - E_{Dim}^a = (H_{D1}^{Form} + H_{Ag}^{Form}) - (H_{D2}^{Form} + H_{Ag_2}^{Form}) + (H_{D1 \cdot AgI}^{Int} - H_{D2 \cdot AgI}^{Int}) \quad (14)$$

E. Comparison with Theory

1. Molecular Origin of the Enhancement:

We have indicated that metallic dimer loss dominates the evaporation channels we are presently studying in the pure metallic cluster ions (Ag_5^+ , Ag_7^+ , and Ag_{11}^+). For these clusters, since AgI is not present, the last term on the right hand side of equation 14 is absent and one might conclude that for pure metallic clusters:

$$E_{\text{Mon}}^a - E_{\text{Dim}}^a = (H_{\text{D1}}^{\text{Form}} + A_{\text{g}}^{\text{Form}}) - (H_{\text{D2}}^{\text{Form}} + H_{\text{Ag2}}^{\text{Form}}) \\ = +A \quad \dots \dots \dots (15)$$

If one assumes similar frequency factors for the metallic monomer and dimer evaporation processes, then A must be a positive number since E_{Mon}^a would be $> E_{\text{Dim}}^a$. The dipole/induced-dipole term (the last term on the right hand side) in equation 14 has the form:

[illegible]

If α_{D1} is $> \alpha_{D2}$, this term becomes negative and tends to decrease the difference between the activation energy for the monomer and dimer evaporation i.e. would enhance monomer evaporation. Our theoretical results of calculating the polarizabilities of the silver cluster ions using density functional within the local density approximation (see Appendix I) are shown in Fig. 5. According to this figure, α increases smoothly as the number of electrons increases. Thus $\alpha_{D1} > \alpha_{D2}$ which makes the last term on the right hand side of equation (14) negative. This we believe is the molecular origin of the enhancement of the monomer evaporation by the dipolar AgI molecules in these clusters. Combining equations 14, 15, and 16

one gets for the (mixed) clusters: $E_{\text{Mon}}^a - E_{\text{Dim}}^a = A - B$. Thus comparing the enhancement in different clusters depends on the relative size of these two terms.

2. Comparison of Enhancement in Different Clusters:

Equation (14) can be rewritten in the form:

$$\Delta H_{\text{Mon-Dim}}^{\text{Evap}} = E_{\text{mon}}^a - E_{\text{Dim}}^a = \Delta H_{D_1-D_2}^{\text{Form}} + \Delta H_{\text{Mon-Dim}}^{\text{Form}} + \Delta H_{D_1(\text{AgI})-D_2(\text{AgI})}^{\text{Int}} \quad (17)$$

where $\Delta H_{\text{Mon-Dim}}^{\text{Evap}}$ is the difference in the enthalpy of evaporation of metallic monomer and metallic dimer, $\Delta H_{D_1-D_2}^{\text{Form}}$ is the difference in the enthalpy of formation of $[\text{Ag}_{X-1}]^+(D_1)$ and $[\text{Ag}_{X-2}]^+(D_2)$, $\Delta H_{\text{Mon-Dim}}^{\text{Form}}$ is the difference in the enthalpy of formation of Ag and Ag_2 and ΔH^{Int} is the difference in the interaction energy of AgI with D_1 and D_2 . Since $H_{\text{Ag}}^{\text{Form}}$ is the standard enthalpy of formation of atomic silver, i.e. 0.0 eV, and $H_{\text{Ag}_2}^{\text{Form}}$ is the bond energy of Ag_2 , then $\Delta H_{\text{Mon-Dim}}^{\text{Form}} = +1.69 \text{ eV}$.³⁰ If we assume that μ_{AgI} and R are the same in $[(\text{Ag}_{X-1})^+(\text{AgI})]$ and $[(\text{Ag}_{X-2})^+(\text{AgI})]$ then Eq. 14 becomes:

$$E_{\text{Mon}}^a - E_{\text{Dim}}^a = \Delta H_{\text{Mon-Dim}}^{\text{Evap}} = H_{D_1-D_2}^{\text{Form}} + 1.69 \text{ eV} + C(\Delta\alpha_{D_1-D_2}) \quad (16)$$

where $C = -\mu_{\text{AgI}}^2/4\pi\epsilon_0 R^6$ and $\Delta\alpha_{D_1-D_2}$ is the difference in the polarizabilities of $[\text{Ag}_{X-1}]^+$ and $[\text{Ag}_{X-2}]^+$.

The difference in the polarizabilities of $[\text{Ag}_4]^+$ and $[\text{Ag}_3]^+$ designated by $\Delta\alpha_{4-3} = +49.18 \text{ a.u.}^3$. The difference in the polarizabilities of $[\text{Ag}_6]^+$ and $[\text{Ag}_5]^+$ is $\Delta\alpha_{6-5} = +35.20 \text{ a.u.}^3$. The difference in the polarizabilities of $[\text{Ag}_{10}]^+$ and $[\text{Ag}_9]^+$ is $\Delta\alpha_{10-9} = +46.50 \text{ a.u.}^3$. According to equation (17) above positive value for $\Delta\alpha$ enhances the evaporative loss of Ag

monomer. The larger values for $\Delta\alpha_{4-3}$ and $\Delta\alpha_{10-9}$ compared to $\Delta\alpha_{6-5}$ reflect the significant decrease in the polarizability of jellium clusters which have a SJM shell closing, i.e. $[\text{Ag}_3]^+ (1s^2)$ and $[\text{Ag}_9]^+ (1s^2, 1p^6)$. Our results are summarized in Table II.

In examining Table II, we do not observe a proportional relationship between the magnitude of $\Delta\alpha$ and the magnitude of Ag monomer loss. For example, although $\Delta\alpha_{4-3}$ is relatively large, Ag monomer loss for $[\text{Ag}_5(\text{AgI})]^+$ is relatively small compared with $[\text{Ag}_7(\text{AgI})]^+$ and $[\text{Ag}_{11}(\text{AgI})]^+$. This lack of linear correspondence may be explained if we examine all the variables that affect the intensity of a metallic evaporative channel in metastable $[\text{Ag}_{X=5,7,11}(\text{AgI})]^+$ clusters. $\Delta H_{D_1-D_2}^{\text{Form}}$ in Eq. 17, is dependent on $H_{\text{Ag}_{X-1}}^{\text{Form}}$ and $H_{\text{Ag}_{X-2}}^{\text{Form}}$, i.e. the stabilities of $[\text{Ag}_{X-1}]^+$ and $[\text{Ag}_{X-2}]^+$, respectively. A qualitative estimate of the relative stabilities of $[\text{Ag}_{X-1}]^+$ and $[\text{Ag}_{X-2}]^+$ for $[\text{Ag}_{X=5,7,11}]^+$ can be made from a comparison of the relative mass peak intensities of $[\text{Ag}_3]^+$ and $[\text{Ag}_4]^+$, $[\text{Ag}_5]^+$ and $[\text{Ag}_6]^+$, and $[\text{Ag}_9]^+$ and $[\text{Ag}_{10}]^+$, respectively, in the "normal" scan spectrum of Figure 4. The greater stability of $[\text{Ag}_3]^+$ compared with $[\text{Ag}_4]^+$, as reflected from its greater intensity in Figure 4, may largely cancel the greater polarizability of $[\text{Ag}_4]^+$ compared with $[\text{Ag}_3]^+$ as shown in Figure 5. As a consequence, although $\Delta\alpha_{4-3}$ is relatively large (making $\Delta H_{(\text{Ag}_4^+)(\text{AgI})-(\text{Ag}_3^+)(\text{AgI})}^{\text{Int}}$ large and negative), it may be cancelled by an equally large positive value for $\Delta H_{(\text{Ag}_4^+)-(\text{Ag}_3^+)}^{\text{Form}} + 1.69\text{eV}$. Further theoretical calculations or experimental measurements of the binding energies of $[\text{Ag}_x]^+$ clusters are necessary to quantitatively verify these conclusions. Unfortunately, recent high level theoretical calculations of the binding energies of $[\text{Ag}_x]^+$ clusters³¹ are not, as yet, consistently accurate to predict the dominant evaporative channel of metastable $[\text{Ag}_{X=\text{odd}}]^+$ clusters. We will address this issue in a forthcoming publication.³²

To summarize: For metastable $[\text{Ag}_{X=5,7,11}(\text{AgI})_{Y=0-4}]^+$ clusters, the probability of an evaporation channel reflects the relative stability of the products of competing channels. The evaporative channels of metastable $[\text{Ag}_x]^+$ clusters are dependent on one physical property of the cluster: metallic stability. We have shown that dipole/induced-dipole forces between dipolar AgI

molecules and the polarizable Jellium metallic cluster enhances monomer evaporation in metallic clusters for which dominance of dimer evaporation is observed. We suggest that the polarizability of the metallic part (which determines the size of the induced-dipole) determines the strength of the dipole/ induced-dipole forces binding the dipolar AgI molecules to the metallic part of the cluster. The oscillation in the probability of the Ag monomer loss for $[\text{Ag}_x(\text{AgI})_{Y=\text{odd}}]^+$ vs. $[\text{Ag}_x(\text{AgI})_{Y=\text{even}}]^+$ is consistent with the suggested mechanism. The contribution of cluster configurations with dipole "pairing" in metastable $[\text{Ag}_{x=5,7,11}(\text{AgI})_{Y=\text{even}}]^+$ clusters leads to a smaller effective permanent dipole moment, a reduced the dipole-induced-dipole forces and thus a decrease in the enhancement factor for monomer loss in these clusters.

APPENDIX I. THEORETICAL MODEL: DENSITY FUNCTIONAL THEORY

The ground state electronic structure of the clusters is obtained by solving self-consistently the Kohn-Sham density functional equations^{33,34} for the valence electrons in an effective potential

$$\left\{ -\frac{1}{2}\nabla^2 + V_{eff}(r) \right\} \phi_i = \varepsilon_i \phi_i, \quad n(r) = \sum_{i=e}^N |\phi_i(r)|^2, \quad (5)$$

where ε_i, ϕ_i are the Kohn-Sham eigenvalues and wave function respectively, $n(r)$ is the total electronic density of the cluster, and

$$V_{eff}(r) = V_H(r) + V_{xc}(r) + V_{jel}(r), \quad (6)$$

where V_H is the electrostatic Hartree potential, V_{xc} is the exchange-correlation potential in the local density approximation (LDA) using the Gunnarsson-Lunqvist functional,³⁵ and V_{jel} is the potential created by a spherical distribution of positive charge $n_+(r) = n_+^0 \Theta(R-r)$, where n_+^0 is the homogeneous metallic density of the material, R is the radius of the cluster that is linked to the number N of atoms by the relation $4\pi R^3/3 = \Omega N$ being the volume per atom Ω assumed equal to that of the pure metal, and $\Theta(r)$ is the step function. This spherically symmetric potential leads to a simplification of the calculations. SJM reproduces very well the shell structure or magic numbers observed in the abundance mass spectra of a variety of metallic clusters.¹ This shell structure is associated with the filling of the spherical electronic shells $1s^2, 1p^6, 1d^{10}, 2s^2, 1f^{14}, 2p^6, \dots$ and electronic supershells.³⁶ Also other electronic properties such as ionization potentials, electron affinities and fragmentation channels have been successfully described in this model.^{17,37}

The Density Functional Theory is a well founded theory for the ground state properties, but no theoretical framework has been established for the case of excited states. Within this theory the calculation of the static polarizability is exact in the sense that it can be obtained from two ground state calculations, by solving the Kohn-Sham equations for the system with and without the external applied field. This method has been used to study the polarizabilities of sodium clusters;¹⁰ good agreement with experiments was found. The main problem of this method is that it is computationally cumbersome and it is difficult to apply to large sized clusters. In this work, instead of solving the equations in the presence of the external field, we will apply first order perturbation theory. This allows us to perform the full calculation keeping the simplicity of the spherical symmetry of the ground state; then the polarizability can be calculated by solving the so called Sternheimer equations.^{12,38} This approach is equivalent to time-dependent linear-response theory in the limit of $\omega=0$.³⁹ We will adopt this approach here to study the optical polarizability dipolar external field ($V_{ext}(\vec{r}, \omega) = rY_{10}$), that is, we use the Time-Dependent Density-Functional Theory within the LDA approximation for exchange and correlation (TDLDA), which has been used successfully to study optical properties of atoms,³⁹ metallic clusters^{40,41} and fullerenes.⁴² In this linear response theory the dynamical screening properties are studied through the interacting electronic susceptibility χ , which is obtained from the time-independent single-particle susceptibility χ_0 and the functional derivative of the effective potential $K(\vec{r}_1, \vec{r}_2) = \delta V_{eff}(\vec{r}_1) / \delta p(\vec{r}_2)$ assumed to be time-independent. By solving the Dyson-type integral equation

$$\chi(\vec{r}_1, \vec{r}_2, \omega = 0) = \chi_0(\vec{r}_1, \vec{r}_2, \omega = 0) + \int \chi_0(\vec{r}_1, \vec{r}_3, \omega = 0) K(\vec{r}_3, \vec{r}_4) \chi(\vec{r}_4, \vec{r}_2, \omega = 0) d\vec{r}_3 d\vec{r}_4. \quad (7)$$

χ_0 is constructed via the eigenvalues ϵ_i , wave functions ϕ_i , and retarded one-electron Green's functions corresponding to the self-consistent effective potential of the ground state Kohn-Sham calculation (eq.(6)). Through the kernel, K , in the Dyson equation the local field effects are included in the calculation of the interacting susceptibility^{12,41} and through the spherical Green's

function we include all the continuum states in our calculation. Then the dipolar static polarizability $\alpha(0)$ is given by

$$\alpha(0) = \int V_{ext}(\vec{r}_1) \chi(\vec{r}_1, \vec{r}_2, \omega = 0) V_{ext}(\vec{r}_2) d\vec{r}_1 d\vec{r}_2. \quad (8)$$

The SJM we have applied is strictly speaking well defined for closed shell clusters. For open-shell clusters, the electronic density is no longer spherically symmetric and both the ground state Kohn-Sham equations as well as the calculation of the Green's functions becomes much more difficult. In order to keep the spherical symmetry in this case, we follow the proposal of Manninen⁴³ and calculate the polarizability using fractional occupation numbers for the degenerate levels. Within this simplified model we will not get the fine details such as the evolution of polarizability with size, but since experimentally the measured polarizability is an average value¹ this model should give reasonable estimates.¹² The reliability of SJM for alkaline sodium clusters has been shown in the literature.^{1,44} The values of the optical dipolar polarizabilities¹² follows not only the experimental trends and also the real values.⁷ In the case of silver clusters, no experimental data is available at this time, and the behaviour of the collective resonance frequencies^{8,11,45} for large cluster sizes suggest that there is an effect of the inner d-core silver electrons on the resonance frequency. However this effect is decreasingly important as we go to smaller cluster sizes.¹¹ SJM has been able to accurately reproduce the shift in the plasma resonance of small silver clusters embedded in inert matrices when we change the matrix.⁴⁶ Besides that, the shell structure observed in field-emission spectra of gold-clusters⁴⁷ as well as the good agreement for some electronic properties on silver clusters³⁷ gives support to the applicability of SJM to small silver clusters. Hence in the present calculations, we expect small errors to arise from neglecting the contribution of the core polarization effects on the optical polarizability.

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FIGURES

FIG. 1. Relative evaporative channels for the unimolecular dissociation of metastable $[\text{Ag}_5(\text{AgI})_{Y=0-3}]^+$ clusters (top panel). Relative *metallic* evaporative channels for metastable $[\text{Ag}_5(\text{AgI})_{Y=0-3}]^+$ clusters (middle panel). Ag monomer loss per AgI (bottom panel).

FIG. 2. Relative evaporative channels for the unimolecular dissociation of metastable $[\text{Ag}_7(\text{AgI})_{Y=0-3}]^+$ clusters (top panel). Relative metallic evaporative channels for metastable $[\text{Ag}_7(\text{AgI})_{Y=0-3}]^+$ clusters (middle panel). Ag monomer loss per AgI (bottom panel).

FIG. 3. Relative evaporative channels for the unimolecular dissociation of metastable $[\text{Ag}_{11}(\text{AgI})_{Y=0-4}]^+$ clusters (top panel). Relative metallic evaporative channels for metastable $[\text{Ag}_{11}(\text{AgI})_{Y=0-4}]^+$ clusters (middle panel). Ag monomer loss per AgI (bottom panel).

FIG. 4. Typical "normal" scan mass spectra of stable $[\text{Ag}_x]^+$ clusters (Ref. 19a). Note shell closings ("magic" numbers) at $[\text{Ag}_3]^+$ ($1s^2$) and $[\text{Ag}_9]^+$ ($1s^2, 1p^6$). Odd/even oscillation for "open" shell clusters are also prominent. $[\text{Ag}_{X=5,7,11}]^+$ are marked by an asterisk.

FIG. 5. Local Density Approximation calculation of the Spherical Jellium Model polarizability of $[\text{Ag}_x]^+$ clusters as a function of cluster size.

TABLES

TABLE I. Relative evaporative channels from the unimolecular dissociation of metastable $[Ag_{X=5,7,11}]^+$ clusters in the 1st FFR at 10.16b kV acceleration. SJM electronic configurations are shown for the parent ion, daughter ion and neutral fragment. A SJM "closed" shell configuration is denoted by CS and indicates a cluster of high stability.

<i>Parent Ion</i>	<i>Daughter Ions</i>	<i>Evap. Ratio</i>
1.) $[Ag_5]^+(1s^2 1p^2)$	$\rightarrow [Ag_3]^+(1s^2 / CS) + Ag_2(1s^2 / CS)$	96.7%±0.3%
	$\rightarrow [Ag_4]^+(1s^2, 1p^1) + (1s^1)$	3.3%±0.3%
2.) $[Ag_7]^+(1s^2 1p^4)$	$\rightarrow [Ag_5]^+(1s^2, 1p^2) + Ag_2(1s^2 / CS)$	98.5%±0.4%
	$\rightarrow [Ag_6]^+(1s^2, 1p^3) + Ag(1s^1)$	1.5%±0.4%
3.) $[Ag_{11}]^+(1s^2 1p^6, 1d^2)$	$\rightarrow [Ag_9]^+(1s^2, 1p^6 / CS) + Ag_2(1s^2 / CS)$	97.0%±0.4%
	$\rightarrow [Ag_{10}]^+(1s^2, 1p^6, 1d^1) + Ag(1s^1)$	3.0%±0.4%

TABLE II. The effect of AgI on the percentage of Ag monomer loss and the difference in the polarizabilities of the silver daughter ions formed upon monomer and dimer evaporation.

Parent Ion	$\Delta\text{Ag Loss}$	$\Delta\alpha$
1.) $[\text{Ag}_x=5(\text{AgI})]^+$	$8.9\% \pm 8.7\%$	$\Delta\alpha_{4-3} = + 49.18 \text{ a.u.}^3$
2.) $[\text{Ag}_x=7(\text{AgI})]^+$	$36.9\% \pm 4.4\%$	$\Delta\alpha_{6-5} = + 35.20 \text{ a.u.}^3$
3.) $[\text{Ag}_x=11(\text{AgI})]^+$	$23.2\% \pm 0.9\%$	$\Delta\alpha_{10-9} = + 46.50 \text{ a.u.}^3$

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